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(54) Title: REDUCED DUST LUBRICANT AND PROCESS FOR PREPARATION OF METALS FOR COLD FORMING (57) Abstract Release of dust into the environment when using conventional stearate soap lubrication for cold working of metals over a phosphate conversion coating can be greatly reduced by adding to a conventional stearate soap lubricating solution an effective amount, e.g., up to 25 weight percent of a water-soluble alkali metal soap of an unsaturated fatty acid, i.e. oleic acid. Optionally, a film forming polymer to further reduce any dust, along with optional corrosion inhibitors and/or complexing agents for heavy metals.		

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REDUCED DUST LUBRICANT AND PROCESS FOR PREPARATION OF METALS FOR COLD FORMING

Field of the Invention

The present invention relates to compositions and methods for lubricating metal surfaces prior to drawing or other cold forming processes on the lubricated metal. Normally, the surfaces to be lubricated are first given a phosphate conversion coating, before applying the lubricant according to this invention.

Statement of Related Art

It has been known for many years to prepare metals for cold forming by lubrication with a soap or similar material. Generally, a phosphate conversion coating, applied from solutions that contain zinc ions, and sometimes also contain calcium, nickel, manganese, copper, and/or other divalent metal ions, is put on the surface prior to coating with the soap. An aqueous solution of alkali metal soap, such as sodium stearate, capable of reacting with zinc phosphate to produce a very favorable form of zinc stearate called "reacted lube" in situ on the surface, is generally preferred for the lubrication stage.

The outer surface of a metal object treated with such a lubricant has a thin, friable layer of soap on it, and any physical handling of such an object, including the drawing processes for which they have been lubricated, often generates dust in the surrounding atmosphere. Increased general consciousness in recent years about chronic illnesses possibly caused by workers breathing dusts has motivated attempts to change or modify soap type lubricants used before cold forming, to reduce the generation of dust from metal objects so treated. Such is one object of this invention.

Published European patent application 0 301 120, according to an English abstract of it, teaches a metal working lubricant composition comprising (A1) 0.2 - 1.8% by weight of poly(vinyl alcohol) and/or (A2) 0.2 - 3% of a derivative of polyvinyl alcohol produced by treating the poly(vinyl alcohol) with an oxidizing agent and containing, in addition to -OH groups, keto groups, carboxyl and/or carboxylate ion groups and optionally aldehyde groups and/or olefin groups conjugated with keto groups, (B1) 1 - 45% of water-insoluble fatty acid salts of which at least 65% have a chain length of at least 16 carbon atoms and (B2) 0 - 1.5% of water-soluble alkali metal soaps, and/or (C1) 1 - 6% of a glass-forming borate and/or (C2) 1 - 6% of boric acid esters of polyvinyl alcohols (A1) and/or (A2), and (D) 0 - 1% of a surfactant.

An English abstract of published East German patent application 257 359 teaches a lubricant for cold working of metal comprising 1 - 45% of an alkaline earth metal soap, 0.2 - 1.8% of poly(vinyl alcohol), 4 - 6% alkali metal borate, and the balance water.

An English abstract of published East German patent application 256 804 teaches a lubricant for cold working of metal comprising insoluble soaps dispersed in water, glass-forming inorganic additives, poly(vinyl alcohol), and optionally surfactants, wherein 0.2 - 3% of the

solution is a derivative of PVA structurally modified by an oxidant so that it contains at least keto and carboxyl or carboxylate groups.

5 An English abstract of a Russian patent application SU-279841, describes a lubricant for cold drawing of metals comprised of an alkali metal soap of a composition containing 25-50% by weight of oleic acid, 5-10% stearic acid, 15-20% linoleic acid and 5-10% dihydroxy stearic acid, the balance being polymerization products, 10 triglycerides and esters of the acids.

None of the abstracts of these East German, Russian and European patents teach any dust reduction benefits from using the compositions taught therein.

15 Japanese Laid-Open Application 57-40200 teaches that exfoliation and shedding of a lubricant layer during cold drawing may be substantially reduced by adding 2 - 5 % of an emulsion of a copolymer of ethylene and vinyl acetate to a lime soap lubricating solution containing quick lime, metal soap, aluminum stearate, and water or to a 20 solution of borax and water. The presence of quicklime (i.e., calcium oxide or hydroxide) in the solutions according to this invention would destroy reacted lube.

Description of the Invention

25 In this description, except in the operating examples or where expressly stated to the contrary, all numbers describing amounts of materials or conditions of reaction or use are to be understood in all instances as modified by the word "about" in defining the broadest scope of the invention. Practice within the exact 30 numerical limits specified is generally preferred.

35 An improved fatty acid soap lubricant composition has now been discovered in which the dust generating tendency is greatly reduced in use in cold forming processes of lubricated metals. The improved soap lubricant component of the lubricant composition consists essentially of an alkali metal salt of a saturated fatty acid with up to about 25 weight percent of an alkali

metal salt of an unsaturated fatty acid. As little as about 2.5% by weight of the unsaturated fatty acid salt provides some improvement in dust reduction, with from 5-25% being more desirable and from about 10 to 15 or 22% being most preferred. Typically the alkali metal salts are the sodium, potassium or lithium salts, with sodium being preferred.

While fatty acids, saturated and unsaturated, having 8 to 22 carbon atoms may be employed, the preferred acids are those with 16-20 carbon atoms with the 18 carbon atom acids being most preferred. Thus, sodium stearate soap is the most preferred for the saturated fatty acid component with sodium oleate being preferred as the unsaturated fatty acid component.

In view of the foregoing, there is provided a lubricant for cold forming of metals comprised of a fatty acid soap component, an improvement for providing reduced dust tendency wherein the improvement is a fatty acid soap component consisting essentially of a mixture of an alkali metal soap of a saturated fatty acid having from 8 to 22 carbon atoms (most preferably 18 carbon atoms) and up to 25% by weight (more desirably 5-22%, and preferably 10 to 15 or 22%) of an alkali metal soap of an unsaturated fatty acid having from 8 to 22 carbon atoms (most preferably 18 carbon atoms).

The fatty acid soaps are water soluble, also called reactive soaps as they react with the zinc phosphate conversion coatings typically employed on the metal surfaces prior to application of the lubricant composition before cold drawing or forming of the metal. The typical reactive saturated fatty acid soap available is sodium stearate, a technical grade available commercially as C_{18} soap containing at least 95% sodium stearate, with < 3% of C_{16} fatty acids, and < 1% combined C_{15} and C_{17} fatty acids. Grades containing lesser amounts of sodium stearate may be employed but are less desirable.

It is preferred that the concentration of reactive soap in the working lubricant solutions according to the invention lie within the range of 5 to 150 g/L of solution. Increasingly more preferably, the amount of reactive soap concentrate is at least 10 or 16 g/L, up to about 60 or 70 g/L.

It is preferred that the lubricant solutions according to this invention should be substantially free from insoluble soaps such as the alkaline earth metal and other polyvalent metal ion salts of fatty acids. Less than 1% by weight, or with increasing preference, less than 0.8, 0.5, or 0.1% by weight of such insoluble soaps are preferred in the compositions.

The dust generating tendency of the soap lubricant coatings may be further reduced, without substantial loss of lubricating effect, by addition of an optional water-soluble, film-forming polymer to the aqueous solution from which the lubricant coating is conventionally applied, as further described in commonly assigned, U.S. application of Kulongowski, U.S. Serial No. 551,982, filed July 12, 1990. (The term "water-soluble" as used for the film-forming polymer herein means that the solubility is sufficient to cause an appreciable reduction in dusting tendency when used together with other conventional ingredients in a conventional aqueous, post-phosphating, lubricating solution. The term film-forming means that a layer no more than 2 millimeters ("mm") thick of a water solution of the polymer alone dries spontaneously at a temperature of 85° or more to produce a continuous film. It is increasingly preferable when a continuous film is formed under these conditions at drying temperatures not lower than 72, 60, 44, 31, or 20° C.)

Preferably the amount of water-soluble film-forming polymer used is from 2 to 20, more preferably from 5 to 15, still more preferably from 6 to 8% by weight of the amount of water-soluble salts of fatty acids that are

used in the lubricating solutions.

Preferably, the water-soluble film-forming polymer used for the invention is selected from the group consisting of poly(vinyl alcohol) (hereinafter "PVA"), poly(2-ethyl-2-oxazoline) (hereinafter "PEOx"), poly(ethylene oxide) (hereinafter "PEO"), poly(vinyl pyrrolidone) (hereinafter "PVP"), and copolymers of vinyl acetate and ethylene (hereinafter "EVA"). Among this group, EVA is less preferred and PVA is most preferred, and among types of PVA, that prepared by hydrolyzing poly(vinyl acetate) and containing 11 - 13 % of residual acetate groups is most preferred.

In some cases in which soap solutions according to the invention with water-soluble film-forming polymer as an optional ingredient added to a fatty acid soap formulation, increased corrosion of the coated metal may be observed. This corrosion can be avoided by adding an optional inhibitor to the mixture. Such use of an optional inhibitor is accordingly preferred with use of the optional film-forming polymers. When employed the inhibitor preferably is used in an amount that is from 0.9 to 8.6, more preferably from 1 to 7, still more preferably from 2 to 5 weight percent of the amount of water-soluble salts of fatty acids with from 8 to 22 carbon atoms that are used in the lubricating solutions. Preferably the corrosion inhibitor is selected from the group consisting of alkali metal nitrites, organic amines, amine borates, organic carboxylic acids, aromatic sulfonic acids and their water-soluble salts, water soluble salts of boric acid, alkanol amides, and imidazoline. The most preferred corrosion inhibitor is sodium nitrite.

It has also been observed that best results are obtained with soap solutions when they are formulated with the optional film formers that they have somewhat higher Babcock Numbers than would normally be used for the same solution in the absence of the film-forming

polymers. Preferably the Babcock Number in an aqueous soap solution of this invention is between 0.5 and 5, or more preferably between 2 and 3.5.

5 A solution according to this invention may also contain an optional complexing agent for heavy metals, as taught generally in U. S. Patent 4,199,381 of April 22, 1980 to Nuss et al. The complexing agent may be any material known as such in the art, including ethylene diaminetetraacetic acid (hereinafter "EDTA") and its
10 salts, nitrilotriacetic acid (hereinafter "NTA") and its salts, N-hydroxyethylethylene diaminetriacetic acid (hereinafter "NEDTA") and its salts, diethylene triamine pentaacetic acid and its salts, and diethanol glycine.

Alkalinity of a working lubricating solution
15 generally increases removal of any pre-applied phosphate conversion coating layers and increases the tendency of the final lubricant coating to cause dust. Therefore, it is increasingly preferred that the pH of the working lubricating solution according to this invention not
20 exceed 11, more desirably not exceed 10.6, and preferably not exceed 10.0 or 9.6. Most preferably, aqueous lubricating solutions according to the invention have a free acid value as defined hereafter between 0.3 and 0.6 points.

25 Another embodiment of this invention is a composition of a concentrate from which a lubricating solution composition according to the invention can be prepared by mixing with water. Generally, for economy in shipping, a solid concentrate with relatively little
30 (less than 40% by weight) water is preferred. In order to solubilize the preferred amount of the reactive soap from the concentrate and form a working lubricating solution according to the invention, the water with which a solid concentrate is mixed must usually be raised to
35 about 85° C or higher in temperature. As noted earlier, a working lubricant solution will contain from 5 to 150 g/L, preferably 10-16 up to about 60-70 g/L.

A process embodiment of this invention may be performed by contacting a suitable phosphated surface with a lubricating solution according to the invention, as generally described above.

5 An ideal lubricating process would maintain a consistent, high coating weight level of reacted lube, avoid the introduction into the lubricating solution of byproducts that interfere with the desired reaction
10 between constituents of the phosphate coating and constituents of the lubricating solution, and remove a minimal amount of the phosphate coating that was on the metal when it entered the lubricating solution. No
15 actual lubricating solution known can accomplish such ideal lubrication, but preferable prior art practical baths tend toward maximizing the ratio of reacted lube
20 coating weight to conversion coating loss, with consideration toward optimizing the ratio of reacted lube coating weight to unreacted lube coating weight. In the present invention, it has been found that the amount of
25 reacted lube is less important than with solutions of the prior art, because sufficiently low drawing forces and adequate lubrication for drawing can be obtained with lower ratios of reacted to unreacted lube than in the prior art. Nevertheless, it is increasingly preferred
30 that a process according to this invention continue for a sufficient time to produce a total lubricant coating weight of at least 3 g/m², in order to avoid undesirably high drawing force requirements for the lubricated surfaces produced.

35 The temperature of the lubricating solution and the time of contact between the lubricating solution and the phosphated surface in any process according to this invention are generally within the range of such conditions as used in the art for reactive lubrication. For example, the temperature is usually preferably
40 between 70 and 90° C, more preferably between 76 and 87° C, and the time of contact is preferably between 1 and 10

minutes, more preferably between 3 and 7 minutes.

Other variables investigated had relatively little effect on the results. No difference in dusting tendency was observed between final drying at room temperature and at 121° C for from 10 to 15 minutes. Also, no difference in dusting tendency was apparent when phosphate conversion coating levels were varied from 10.8 to 21.6 grams per square meter ("g/m²"). There was a slight increase in dusting tendency when the phosphate coating was as light as 3 g/m², so that it is preferred that the phosphate coating exceed that value.

The practice of the invention may be further appreciated with the help of the following non-limiting operating examples and comparison examples.

General Conditions for All the Examples and Comparative Examples

The temperature of the lubricating solutions was maintained at 79° C, and phosphated metal specimens were contacted with the solution for 5 minutes, then dried for 15 minutes in an oven maintained at between 88 and 99° C. The test specimens were Type 1010 cold rolled steel that had been conventionally alkaline cleaned, pickled in sulfuric acid, and phosphated by use of one of the commercial zinc phosphating solutions available from the Parker+Amchem Division of Henkel Corporation, Madison Heights, Michigan, under the trade mark Bonderite™. Two different types of Bonderite™ were used, in solutions maintained with a total acid number of 35 points, with no significant difference in the results as reported below. (Points in this instance are defined as the number of milliliters of 0.1 N NaOH solution required to titrate a 5 ml sample of the phosphating solution to a phenolphthalein end point.) The average phosphate coating weight was 12 grams per square meter of surface (hereinafter "g/m²") for all the panels.

The free acid content of the lubricating solutions was measured according to the following procedure:

Free Acid

5 Pour 200 ml of a solution of 0.2 weight
percent phenolphthalein in isopropyl alcohol
into a 400 ml beaker, then add a 10 ml sample
of hot lubricating solution, measured with a
conical graduate or a pipet. Heat the mixture
in the beaker to boiling, and boil for at least
one minute. Remove from heat and titrate
immediately, while the solution is still hot,
10 with 0.1 N NaOH solution if the solution is
clear rather than pink, to the development of a
permanent, faint pink. The ml of titrating
solution required is the number of "points" of
free acid. If the solution is already pink
15 after boiling, titrate with 0.1 N sulfuric acid
instead to the permanent disappearance of the
pink color. The number of ml of acid is then
the points of free alkalinity.

20 The Babcock Number of the lubricating solutions was
measured by the following method:

 Pour 10 ml of a solution of 0.2 weight
percent phenolphthalein in 2-propanol into a 50
ml beaker, then add an accurately measured 10
ml sample of the hot lubricating solution to be
25 measured, mix thoroughly and heat to boiling.
Filter through a fast filter paper such as
Whatman 541 into a Babcock test bottle with a
graduated neck. Wash the beaker and filter
paper with a second 10 ml amount of a solution
30 of 0.2 weight percent phenolphthalein in 2-
propanol that has been heated to boiling just
before use. Discard the filter paper. Place
the Babcock bottle into a boiling water bath
for at least 30 min to drive off all the 2-
35 propanol introduced. Then add 20 ml of a
solution of 50 weight percent sulfuric acid in
water to the Babcock bottle. Swirl the bottle

5 to mix its contents and heat the flask and
contents in a boiling water bath until a
distinct oily layer has formed on top of the
liquid in the flask. Add hot water to the
10 flask if necessary to bring the top and bottom
of the oily top layer within the graduated
portion of the neck of the bottle. The differ-
ence between the graduation values for the
upper and lower edges of the oily top layer is
the Babcock Number for the sample. The Babcock
15 number corresponds to the volume percent of
oily material produced by acidifying the 10 ml
sample of the lubricating solution. Each
Babcock unit corresponds to 2 volume percent of
fatty acids in the lubricating solution. The
20 positions of the upper and lower edges of the
oily layer should be read while the bottle is
still immersed in a boiling water bath, to
avoid errors that result from rapid cooling
when the bottle is removed from the bath.

Coating weights and other related characteristics of
the samples are defined and/or were determined as
follows:

25 W1 = Weight (in grams) of panel and phosphate
coating.
W2 = Weight (in grams) of panel, phosphate coating,
and lube coating after exposure to lubricating
solution.
30 W3 = Weight (in grams) of panel after exposure to
phosphating and lubricating solutions, followed
by water strip.

35 Water strip: Immerse panel in boiling
deionized water, in sufficient volume to
provide at least about 4.3 ml of water per
square centimeter of panel surface, for
three minutes. Remove panel and rinse by
immersion in a similar volume of boiling

deionized water for three minutes. Remove rinsed panel and dry in oven, cool to ambient temperature, and weigh.

W4 = Weight (in grams) of panel after exposure to phosphating and lubricating solutions, followed by water strip as above and solvent strip.

Solvent Strip: Place panel in extraction portion of a Soxhlet or similar extractor that accumulates freshly distilled solvent in a container to a specified level, then drains the accumulated solvent, and repeats the cycle. Make sure all panels loaded are completely covered when the container is filled to just below the level that produces drainage. Extract for at least 30 minutes with condensate from a vigorously refluxing mixture of 55 weight percent isopropyl alcohol, 32 weight percent n-heptane, and the balance 2-ethoxyethanol. Remove panel, dry in oven, cool to ambient temperature, and weigh.

W5 = Weight (in grams) of panel after exposure to phosphating and lubricating solutions, followed by water strip and solvent strip as specified above and then by chromic acid strip.

Chromic Acid Strip: Prepare solution by dissolving 800 g of CrO_3 in sufficient water to make 4 liters. Heat solution to 82°C and maintain at that temperature with stirring and thermostatic control. Immerse panel for 5 minutes. Remove panel from hot solution, rinse quickly in cold water, dry with clean compressed air, and weigh.

Surface Area is measured in square meters.

$$A) \text{ Conversion coating loss} = \frac{(W1 - W4)}{\text{Surface Area}}$$

$$B) \text{ Nonreacted lube} = \frac{(W2 - W3)}{\text{Surface Area}}$$

$$C) \text{ Reacted lube} = \frac{(W3 - W4)}{\text{Surface Area}}$$

$$D) \text{ Residual Conversion coating} = \frac{(W4 - W5)}{\text{Surface Area}}$$

$$E) \text{ Total lube} = \text{Nonreacted lube} + \text{Reacted lube}.$$

Corrosion susceptibility of the lubricant coated samples was measured according to American Society for Testing Materials Standard Procedure D2247-87. Results are reported below according to the following scale, from visual observation of the amount of red and/or white corrosion on the sample tested:

	<u>Rating Symbol</u>	<u>Percent of Area of Sample Corroded</u>
	R10	0
20	R9.5	< 10
	R9	10 - < 20
	R8	20 - < 30
	R7	30 - < 60
	R6	60 - < 80
25	R5	80 - 100

The dusting tendency was measured by the following procedure: A square of dark colored velour material 6.5 centimeters ("cm") long on each side was placed in contact with a dried lubricant-coated panel to be tested. The panel was 15 cm long, and the square of velour was initially placed at the top center of the panel. A cylindrical weight with a mass of 1 kilogram and a diameter of about 5 cm was placed in the center of the square of velour and the latter was pulled along the remaining length of the panel while the weight remained

in place. After this traverse of the panel, the light colored dust from the lubricant coating, if present, could easily be seen against the dark velour. The amount of such dust present was rated on a scale of 1 to 10, with 1 corresponding to no visible dust and 10 to complete coverage of the velour within the circular area on which the weight had rested during its traverse of the panel.

The ease of drawing was measured on a "LUB" model draw test machine manufactured by Detroit Testing Machine Company, Detroit, Michigan. A 1/2 inch die was used at clamping forces up to 6000 pounds at increments of 200 pounds. The force required for drawing was read directly from instruments on the machine.

Example 1

A base lubricant solution concentrate was prepared by first mixing 154 parts by weight ("PBW") of 50 % aqueous sodium hydroxide with 359 PBW of additional water and heating the solution to about 75° C. To this mixture was added while stirring, from a melt tank, 526 PBW of a high quality technical grade stearic acid containing > 95% by weight of C₁₈ fatty acid(s), < 3% of C₁₆ fatty acid(s), and < 1% of combined C₁₅ and C₁₇ fatty acid(s). While the melted fatty acids were being added, 5 PBW of pine oil was simultaneously added, from another container, to the mixture with stirring. The mixture was held at temperature with continued mixing until about 45 PBW of water had been lost by evaporation. The mixture was then allowed to cool, forming a friable solid product, containing approximately 57 weight percent sodium salt of fatty acids.

To prepare the base lubricating solutions noted below, an amount of the sodium stearate concentrate prepared as described above was dissolved in water, at a temperature in the range of 74 - 94°C in the amounts of 60-90 g/L noted in the Table 1 below, to which was then added the amounts of oleic acid and NaOH noted to provide

a mixture of sodium stearate and sodium oleate soaps having a Babcock Number of about 2-3 which were then evaluated for dust tendency as described above. The composition of the lubricants evaluated can be seen from the following Table 1A and the results of dusting evaluation seen from Table 1B.

Table 1A

	Lubricant Sample	Sodium Stearate Concentrate (g/L)	Oleic Acid (g/L)	NaOH (g/L)
10	1	60	0	0
	2	60	0.3	.05
	3	60	0.9	.14
15	4	60	2.4	.37
	5	60	9.9	.76
	6	60	9.9	1.5
	7	70	9.9	1.5
	8	80	9.9	1.5
20	9	90	10.0	1.5

Table 1B

	Lubricant Sample	Non- Reacted Lube (Water Soluble) (g/m ²)	Reacted Lube (Solvent Soluble) (g/m ²)	Total Lube (g/m ²)	Residual (g/m ²)	Dust Rating
25	1	6.1	12.3	18.4	14.2	10
	2	6.8	11.6	18.4	13.6	10
30	3	5.5	8.9	14.4	14.1	7
	4	5.6	7.1	12.7	15.3	7
	5	5.8	4.3	10.1	14.2	6
	6	6.8	1.5	8.3	14.7	5
	7	6.1	4.5	10.6	15.0	5
35	8	9.2	5.7	14.9	14.1	4
	9	10.8	7.3	18.1	17.2	4

As can be seen from the foregoing, the total dust level decreases with increased amounts of the sodium oleate with amounts of above about 5% up to about 22% based on the amount of sodium stearate being the most desirable. Based on the total amount of fatty acid soaps, and a total soap level of less than 80 g/L, a level of about 10-22% by weight provides the most desirable results.

Example 2

In this example the ease of drawing was measured on a "LUB" model draw test machine as noted earlier with clamping forces up to 6000 pounds. The force of drawing in pounds is read directly from instruments on the machine.

In the first "LUB" test with a 1/2 inch die, 75 g/L of sodium stearate concentrate as described earlier was employed on metal having a zinc phosphate conversion coating and compared with the same sodium stearate to which was added 7.5 g/L of oleic acid and sufficient sodium hydroxide to neutralize the oleic acid. The sodium stearate lubricant had a dust rating of 10 and the stearate plus oleate lubricant had a dust rating of 5. The draw force and clamping force in lbs. were as follows:

Table 2

	Clamping Force (Lbs)	Draw Force (Lbs.)	
		Sodium Stearate	Sodium Stearate and Oleate
5	1600	170	---
	1800	195	---
	2000	215	150
	2200	235	180
10	2400	265	200
	2600	280	205
	2800	300	225
	3000	320	230
15	3200	325	255
	3400	350	275
	3600	375	265
	3800	450	290
20	4000	600	345
	4200	---	335
	4400	---	385
	4600	---	380
25	4800	---	430
	5000	---	520
	5250	---	510
	5500	---	635

Example 3

In this example another "LUB" test was run again with a 1/2 inch die on zinc phosphate conversion coated metal using sodium stearate concentrate as described earlier.

30 The samples tested were two sets, one employing an old solution of sodium stearate concentrate used previously at a level of 90 g/L compared to the same stearate lubricant to which was added 5.6 g/L of sodium oleate (as sodium oleate, not oleic acid and sodium hydroxide). The

35 second set was carried out using a freshly prepared

sodium stearate lubricant (prepared as earlier described) at a level of 90 g/L compared to the same freshly prepared sodium stearate lubricant to which was added 5.6 g/L sodium oleate (as sodium oleate). The dust rating of the old stearate lubricant was 7, while the old plus the added sodium oleate was 3. The dust rating of the freshly prepared sodium stearate was 10, while the freshly prepared lubricant to which sodium oleate was added provided a dust rating of 3. All solutions had a Babcock Number of 3.

The draw force and clamping results can be seen in the following Table 3.

Table 3Draw Force (Lbs.)

	<u>Clamping Force (Lbs.)</u>	<u>Old Stearate</u>	<u>Old Stearate & Oleate</u>	<u>Fresh Stearate</u>	<u>Fresh Stearate & Oleate</u>
15	3200	400	255	---	---
	3400	400	---	---	280
20	3600	425	295	---	---
	3800	460	---	---	320
	4000	545	350	355	320
	4200	650	---	---	---
	4400	890	400	410	390
25	4600	---	505	---	---
	4800	---	530	---	420
	5000	---	550	535	475
	5250	---	875	1000	795

From the foregoing it can be seen that the dust ratings are significantly improved by the addition of the sodium oleate to a stearate lubricant composition. From Table 3, a significant improvement in drawing is particularly noted with the old, aged lubricant.

What is claimed is:

1. In a water soluble lubricant for cold working of a metal surface comprising a fatty acid soap component, the improvement wherein said fatty acid soap component consists essentially of a mixture of:
 - (A) a water soluble alkali metal soap of a saturated fatty acid having 8 to 22 carbon atoms and
 - (B) a water soluble alkali metal soap of an unsaturated fatty acid in an amount effective to reduce the dusting tendency of said metal surface after coating and drying of said lubricant.
2. A lubricant as defined in claim 1 wherein said fatty acid soap of said unsaturated fatty acid is present in an amount of up to 25% by weight of said fatty acid soap component.
3. A lubricant as defined in claim 2 wherein said amount is about 5 to 22%.
4. A lubricant as defined in claim 2 wherein said amount is about 10 to 22%.
5. A lubricant as defined in claim 1 wherein said saturated fatty acid and said unsaturated fatty acid is a C₁₈ fatty acid.
6. A lubricant as defined in claim 5 wherein said unsaturated fatty acid is oleic acid and said saturated fatty acid is stearic acid.
7. A lubricant as defined in claim 6 wherein said oleic acid soap is present in an amount of about 10 to 18 weight percent of said fatty acid soap component.
8. A composition which can be mixed with water to form a liquid working lubricant composition having a pH not greater than 11, for coating a metal surface to reduce the frictional resistance encountered during cold working of the metal surface, comprising water in an amount to dissolve a fatty acid soap component, said fatty acid soap component consisting essentially of a

mixture of:

- (A) an alkali metal soap of a saturated fatty acid having from 8 to 22 carbon atoms and
- (B) a alkali metal soap of an unsaturated fatty acid having from 8 to 22 carbon atoms in an amount effective to reduce the dusting tendency of said metal surface after coating and drying of said lubricant.

9. A composition as defined in claim 8 wherein said alkali metal soap of said saturated fatty acid is sodium stearate.

10. A composition as defined in claim 8 wherein said alkali metal soap of said unsaturated fatty acid is sodium oleate.

11. A composition as defined in claim 10 wherein said sodium oleate is present in an amount of about 5 to 22% by weight of said fatty acid soap component.

12. A composition as defined in claim 11 wherein said sodium oleate is present in an amount of about 10-22% and said alkali metal soap of said saturated fatty acid is sodium stearate.

13. A liquid composition for applying a lubricant coating to a metal surface to reduce the frictional resistance encountered during cold working of the metal surface, said liquid composition having a pH not greater than 11 and consisting essentially of water and:

(A) from about 5 - about 150 g/L of a water-soluble fatty acid component consisting essentially of a mixture of:

- (1) an alkali metal salt of a saturated fatty acid having 8 to 22 carbon atoms with
- (2) an alkali metal salt of an unsaturated fatty acid having 8 to 22 carbon atoms in an amount of about 2.5% to 25% by weight of said fatty acid component; and

optionally, one or more of a component selected from the group consisting of:

- (B) a water-soluble film forming polymer;
- (C) a corrosion inhibitor component; and
- 5 (D) a complexing agent for heavy metal ions.

14. A composition as defined in claim 13 wherein said composition has a pH not greater than 10 and a free acid value from about 0.3 to about 0.6 points.

10 15. A composition according to claim 13, wherein the weight of component (B) is from about 2 to about 20% of the weight of component (A).

16. A composition according to claim 14, wherein the weight of component (C) is from about 0.9 to about 8.6% of the weight of component (A).

15 17. A composition as defined in claim 13 wherein said alkali metal salt of said saturated fatty acid is sodium stearate and said alkali metal salt of said unsaturated fatty acid is sodium oleate.

20 18. A composition as defined in claim 17 wherein said sodium oleate is present in an amount of about 5 to 25% by weight of said fatty acid component.

19. A composition as defined in claim 17 wherein said sodium oleate is present in an amount of about 10 to 22% by weight of said fatty acid component.

25 20. A process for reducing the frictional resistance encountered during cold working of a metal surface, wherein the improvement comprises contacting said metal surface, at a sufficient temperature for a sufficient time to deposit a film effective for friction reduction on said metal surface, with the liquid
30 composition defined in claim 13 thereby providing reduced dusting tendency of said metal surface after coating and drying of said liquid composition.

INTERNATIONAL SEARCH REPORT

PCT/US 92/04373

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C10M173/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C10M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,3 915 869 (T.KATONA) 28 October 1975	1-7
Y	see column 1, line 20 - line 45 see column 2, line 34 - line 45 see column 3, line 4 - line 16 see column 3, line 64 - column 4, line 2 see column 6, line 8 - line 13 ---	8-20
Y	GB,A,2 115 001 (DETREX CHEMICAL) 1 September 1983 see claims 1,4,7,9; example 1 ---	8-20
X	US,A,4 752 405 (G.H.KYLE) 21 June 1988	1-7
Y	see column 2, line 41 - line 53; claims 1-29 ---	8-20
	-/--	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 05 OCTOBER 1992	Date of Mailing of this International Search Report 20. 10. 92	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer RO TSAERT L.D.C.	

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	GB,A,2 002 812 (PYRENE CHEMICAL) 28 February 1979 see page 1, line 49 - page 2, line 24; claims 1-5,9-14 -----	8, 13

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9204373
SA 61160

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3915869	28-10-75	BE-A- 724294	02-05-69
		CA-A- 958695	03-12-74
		DE-A- 1810412	03-07-69
		FR-A- 1601458	24-08-70
		GB-A- 1261358	26-01-72
		NL-A- 6816683	27-05-69
		SE-B- 359112	20-08-73

GB-A-2115001	01-09-83	None	

US-A-4752405	21-06-88	CA-A- 1272475	07-08-90
		JP-A- 62263290	16-11-87

GB-A-2002812	28-02-79	DE-A- 2736874	01-03-79
		AT-B- 365224	28-12-81
		AU-B- 521494	08-04-82
		AU-A- 3876878	14-02-80
		BE-A- 869666	12-02-79
		CA-A- 1110611	13-10-81
		FR-A, B 2400398	16-03-79
		JP-C- 1324853	27-06-86
		JP-A- 54035833	16-03-79
		JP-B- 60045273	08-10-85
		NL-A- 7807768	20-02-79
		SE-B- 445044	26-05-86
		SE-A- 7808658	17-02-79
		US-A- 4199381	22-04-80

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